REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 02Nov00	3. REPORT TYPE AND DATES COVERED Final 01Jul97-30Jun00

4. TITLE AND SUBTITLE
Calculations of Intermolecular Potentials Relevant for Defense Research

5. FUNDING NUMBERS
DAAG55-97-1-0174

6. AUTHOR(S)
Krzysztof Szalewicz

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Delaware

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO37010.1-CH-AAS

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Intermolecular forces govern many physical, chemical and biological processes. It is now possible to model such forces on computers using theoretical quantum mechanical methods developed by our group. Recent advances in computer hardware and software allow investigations of typical molecules found in explosives, propellants and solvents. The AASERT grant supported graduate students involved in this research. Their work helped to obtain state of the art potential energy hypersurfaces for various molecules relevant for the defense mission.

14. SUBJECT TERMS	15. NUMBER OF PAGES 4
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

37010 CH-AAS

Calculations of Intermolecular Potentials Relevant for Defense Research

Krzysztof Szalewicz

Department of Physics and Astronomy
University of Delaware
Newark, DE 19716

November 2, 2000

Final report on the Augmentation Award for Science and Engineering Research Training

I. OBJECTIVES

Intermolecular forces govern many physical, chemical, and biological processes. It is now possible to model such forces on computers using theoretical quantum mechanical methods developed by our group. Recent advances in computer hardware and software allow investigations of typical molecules found in explosives, propellants, and solvents. The AASERT grant supported graduate students involved in this research. Their work helped to obtain state of the art potential energy hypersurfaces for various molecules relevant for the defense mission.

II. RESEARCH AND EDUCATION ACTIVITIES

The grant period was 7/1/97 to 6/30/00 and the award amount was $77,689.00. The grant supported mainly a graduate student Eric Mas. In the last year it also supported another graduate student Garol Murdachaev. Both students were involved in various educational activities. These included courses related to their research work taken at the University of Delaware, participation in group meetings which include a significant amount of

pedagogical seminars, and participation in various conferences (mainly Gordon conferences on intermolecular forces). Research activities involved leading edge work on development of intermolecular potentials. The systems studied by the students, described in more detail in the next section, were model systems enabling development of methods applied later by other members of our group to molecules of direct interest to DoD, such as those involved in our SERDP joint project with ARL [1,2]. Eric Mas graduated with a Ph.D. in Physics in May 1999. He is now a postdoctoral associate in the Los Alamos National Laboratory and works on modeling of materials relevant for the US defense mission. Clearly, the training goal of the AASERT program could not have resulted in a better outcome. Garold Murdachaev continues work on his Ph.D. research and is expected to graduate in about three years.

III. RESEARCH ACHIEVEMENTS

Eric Mas work supported by AASERT resulted in three published papers [3–5]. The subject of these papers was the development and testing of intermolecular potentials. Since systems of interest to DoD are very large from the point of view of electronic structure calculations, methods applied to such systems should first be tested on smaller ones. Water was chosen as an excellent test system since it is certainly the most investigated one and therefore comparisons with vast literature data are possible. Furthermore, supercitical water is a subject of significant interest to DoD and first-principles methods should play a particularly important role for condensed phase under extreme pressures and temperatures. Our electronic structure calculations used the symmetry-adapted perturbation theory (SAPT) developed by our group. Iinteraction energies for about 2500 water dimer configurations have been calculated using SAPT. Effective, interaction-optimized bases were used leading to 0.3 kcal/mol accuracy near the minimum of the dimer potential. The computed points were then fitted to two types of analytic potential energy surfaces: a site-site form and an expansion in functions dependent on the vector connecting the centers of mass and on the Euler angles defining the orientation of each monomer. The second virial coefficient was calculated from these surfaces including the quantum correction and isotopic dependence, as well as the molar heat capacity at constant pressure. Comparison of these data to experiment shows that both of our surfaces are superior to any previously available. In addition, the three-body nonadditivity has been computed on a grid of points sufficient for a reduced dimensionality calculation of the water trimer spectra. The dimer spectrum was obtained from the pair potential through rigorous six-dimensional quantum calculations of the vibration-rotation-tunneling (VRT) levels. For the water trimer three-dimensional quantum calculations were performed to reproduce the hydrogen torsional spectrum. The SAPT *ab initio* potentials were found to be the first potentials that quantitatively reproduce the experimental far-infrared spectra of the water dimer. The three-body interactions—together with the pair potential—produce an accurate representation of the hydrogen bond torsional levels in the spectrum of the water trimer. This work indicates that first-principles potentials for water achieved the level of sophistication allowing highly accurate predictions even for observables as sensitive as intermolecular spectra. Thus, one can develop *ab initio* SAPT potentials which can be used to predict properties of materials relevant to the DoD mission such as densities of energetic compounds and properties of supercitical fluids.

Garold Murdachaev continued the work on water with the aim of developing a flexible water potential, i.e., a potential depending on the intramonomer coordinates. This task is beyond reach of the standard *ab initio* methods since the potential energy surface involving all degrees of freedom is 12-dimensional already for the water dimer. However, the SAPT approach allows us to attack this problem by using asymptotic properties of the interaction energy.

REFERENCES

[1] R. Bukowski, J. Sadlej, B. Jeziorski, P. Jankowski, K. Szalewicz, S.A. Kucharski, H.L. Williams, and B.M. Rice "Intermolecular Potential of Carbon Dioxide Dimer from Symmetry-Adapted Perturbation Theory", J. Chem. Phys. **110**, 3785-3803 (1999).

[2] R. Bukowski, K. Szalewicz, and C. Chabalowski "*Ab initio* interaction potentials for simulations of dimethylnitramine solutions in supercritical carbon dioxide with cosolvents", J. Phys. Chem. A **103**, 7322-7340 (1999).

[3] G. C. Groenenboom, E. M. Mas, R. Bukowski, K. Szalewicz, P. E. S. Wormer, and A. van der Avoird "The pair and three-body potential of water", Phys. Rev. Lett. **84**, 4072-4075 (2000).

[4] E. M. Mas, R. Bukowski, K. Szalewicz, G. C. Groenenboom, P. E. S. Wormer, and A. van der Avoird "Water Pair Potential of Near Spectroscopic Accuracy. I. Analysis of Potential Surface and Virial Coefficients", J. Chem. Phys., **113**, 6687-6701 (2000).

[5] G. C. Groenenboom, P. E. S. Wormer, and A. van der Avoird E. M. Mas, R. Bukowski, K. Szalewicz "Water Pair Potential of Near Spectroscopic Accuracy: II. Vibration-Rotation-Tunneling Levels of the Water Dimer", J. Chem. Phys. **113**, 6702-6715 (2000).